SYNTHESIS AND CHARACTERIZATION OF POLYMER-FERROELECTRIC COMPOSITE MATERIAL

A THESIS SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF

Master of Science in **Physics**

By

Subhasmita Swain

DEPARTMENT OF PHYSICS
NATIONAL INSTITUTE OF TECHNOLOGY
ROURKELA – 769008

SYNTHESIS AND CHARACTERIZATION OF POLYMER-FERROELECTRIC COMPOSITE MATERIAL

A THESIS SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF

Master of Science in **Physics**

By

Subhasmita Swain

Under the guidance of

Prof. S.Panigrahi

DEPARTMENT OF PHYSICS
NATIONAL INSTITUTE OF TECHNOLOGY
ROURKELA – 769008

Department of Physics
National Institute of Technology
Rourkela – 769008 (Orissa)

CERTIFICATE

This is to certify that this Thesis entitled "**Synthesis and characterization of Polymer ferroelectric composite material**" submitted by **Subhasmita Swain** in partial fulfilments for the requirements for the award of degree of Master of Science in Physics at National Institute of Technology, Rourkela is an authentic work carried out by her under my supervision and guidance.

To the best of my knowledge, the matter embodied in the project has not been submitted to any other University/ Institute for the award of any Degree or Diploma.

Rourkela
Date: 13.05.2011

Prof. S. Panigrahi
Department Of physics
National Institute Of Technology
Rourkela-769008

ACKNOWLEDGEMENT

Before presenting the thesis work, I would like to mention a few words for the people who gave their complete support for my thesis work.

My first thanks are to the Almighty God, without whose blessings I wouldn't have been writing this “acknowledgments”.

Then I take this opportunity to express my deep regards and sincere gratitude for this valuable, expert guidance rendered to me by guide Prof. S. Panigrahi, Department of Physics, National Institute of Technology Rourkela. I consider me fortunate to have had opportunity to work under his guidance and enrich myself from his vast knowledge and analysis power.

My sincere thanks to Dr. Siddhartha Jena, Professor and Head of Physics Department for his talented advice and providing necessary facility for my work.

I am especially indebted to Dr.Tanmaya Badapanda for teaching me both research and writing skills, which have been proven beneficial for my current research and future career. Without his endless efforts, knowledge, patience, and answers to my numerous questions, this research would have never been possible.

My deep sense of gratitude to PhD Scholar, Mr. Senthil.V, department of Physics, for his valuable suggestions and constant help for this work. He has been very kind and patient while suggesting me the outlines of this project and has clarified all my doubts whenever I approached him.

I record my sincere thanks to Department of Ceramic Engineering, for the help in taking XRD, Department of Metallurgical and Material Science for extending all facilities to carry out the SEM.

I am greatly thankful to all the research scholars of the department and my class mates for their inspiration and help.

Last but not the least; I would like to express my gratefulness to my parents for their endless support, without which I could not complete my project work.

Date :13.05.2011

Subhasmita swain

DEDICATED

TO MY FAMILY AND MY FRIENDS

ABSTRACT

Among all the research fields in material science Polymer Composites are the most rapidly growing one .Polymer Composite materials are adding a great deal of material that is more durable and useful as compared to the conventional material. Ferroelectric ceramics possess high dielectric permittivity but with poor mechanical properties and lower dielectric breakdown strength. By integrating high dielectric permittivity ceramic powder with superior dielectric strength of the polymer, one can develop a composite with high dielectric permittivity and high breakdown strength. This type of composites has high capability of energy storage and can be used in capacitors and energy storage device.

[Ba1-xY2x/3](Zr0.1Ti0.9)O3 powders with different yttrium concentrations (x=0, 0.01, 0.02, 0.03) were Prepared by solid state reaction. These powders were analyzed by X-ray diffraction (XRD). The polymer ceramic composites were prepared using polyvinyl alcohol (PVA) as polymer matrix and Ba1-xY2x/3Zr0.1Ti0.9O3 (BYZT) as ceramics powder by hot pressing technique. The microstructure/surface morphology of the composite was analyzed by scanning electron microscope. Also we have conducted an analysis of the XRD study of Polymer Composites of Poly (vinyl alcohol) with barium titanate. Hot pressed samples are studied the dielectric and impedance spectroscopy.

CONTENTS

		Page no.
Chapter 1	**Introduction**	8
	1.1 Ferro electricity	8
	1.2 Piezoelectricity	9
	1.3 Pyroelectricity	10
	1.4 Pervoskite crystal structure	11
	1.5 Barium Titanate	11
	1.6 Polymer Composite	12
Chapter 2	2.1 Motivation	14
	2.2 Thesis Objective	14
Chapter 3	**Experimental techniques**	15
	3.1 X-ray Diffraction study	15
	3.2 Scanning electron microscope	15
	3.3 Dielectric study	16
	3.4 Impedance study	16
	3.5 Preparation of ceramic powder	17
	3.6 Preparations of Polymer Composite	17
Chapter 4	4.1 Introduction on BZT	19
	4.2 Result and discussion	20
	4.2.1 XRD of BYZT	20
Chapter 5	5.1 Polymer Composite	21
	5.2 Result and Discussion	22
	5.2.1 XRD of Polymer Composite	22
	5.2.2 SEM of Polymer Composite	23
	5.2.3 Dielectric Study of Polymer Composite	24
	5.2.3.1 Temperature dependence of dielectric constant	24
	5.2.3.2 Frequency dependence of dielectric constant	25
	5.2.3.3 Frequency dependence of dielectric loss	26
	5.2.3.4 Complex Impedance spectroscopy	27
Chapter -6	**Conclusion**	29
	References	

CHAPTER-1

1. Introduction:

In the recent years Polymer composite materials have been widely used because of their significant importance. Now the research is rapidly going on ferroelectric composite materials because of their various applications due to their excellent properties. Ferroelectric materials have been of great technological interest due to their excellent properties in various applications. Ferro electricity was first discovered by J.Valasek in 1920.

1.1 Ferro electricity:

When the polarization of the dielectric can be altered by an electric field, it is called ferroelectric. Ferroelectric materials are generally single crystal or polycrystalline ceramic oxides. Ferroelectric materials belong to pyroelectric family. Ceramics are the single crystals because they are easy to synthesize. The first known ferroelectric material found was Rochelle salt in 1921. Then Barium Titan ate (BaTiO3) was discovered to ferroelectric material. In this material the centre of the positive and negative charges does not coincide even without the application of external electric field. It has some properties i.e. they have spontaneous polarization and they exhibit Hysteresis loop. All ferroelectric materials are piezoelectric and pyroelectric but reverse is not possible. The use of ferroelectric materials is RAM for computers, also used in medical ultrasound machine. The ferroelectric materials having domains i.e. the region in which all electric dipoles are aligned in same direction. The variation of polarization with electric field is not linear.

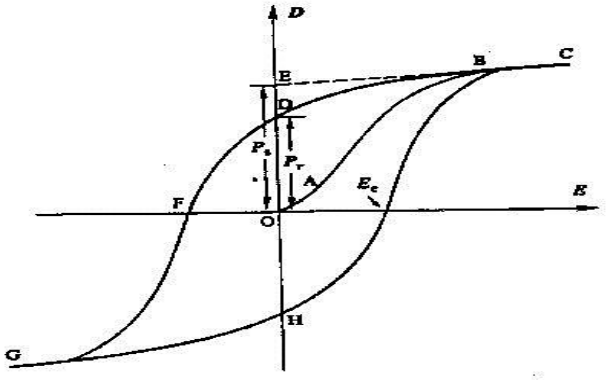

Fig. 1.1: A Polarization vs. Electric Field (P-E) hysteresis loop for a typical ferroelectric crystal.

Here is the P-E loop. We are getting that if we are increasing the field strength the domains start to align in the positive direction which gives rise the increase in polarization. After a certain field the polarization reaches a saturation value. Then if the external field is removed the polarisation does not fall to zero, some polarization is there and this is called remanant polarization. The crystal cannot be completely depolarised until a field of magnitude (OF) is applied and this field is called coercive field (E_c).If the field is increased to more negative value direction of polarisation flips and hence a hysteresis loop is obtained.

1.2 Piezoelectricity:

All ferroelectric materials are piezoelectric. Piezoelectric materials show direct piezoelectric effect and converse effect. i.e these materials having an ability to develop an electrical charge proportional to mechanical stress and a geometrical strain is produced on the application of voltage respectively. It is the interaction between mechanical and electrical state.

$$D = \varepsilon E \text{ (direct effect)}$$

Where D= electric charge displacement vector

E =electric field strength

ε = permittivity

$$S = sT \text{ (converse effect)}$$

Where S=stress

s=compliance

T=strain

Piezoelectric properties are dependent on orientation direction, so they must be described in terms of tensors. i.e.

$$P_i = d_{ij}\alpha_{jk} \text{ (Direct Piezoelectric Effect)}$$

$$\beta_{ij} = d_{ij}E_k \text{(Converse Piezoelectric Effect)}$$

Piezoelectric materials having so many applications i.e. they can be used as transducer, actuator and sensor.

1.3 Pyroelectricity:

The spontaneous polarization which depends upon temperature is called pyroelectric effect. We know that out of 32 crystal classes 11 are centrosymmetry and 21 are non-centrosymmetry and 10 out of 21 are pyroelectric.

$$\Delta P_s = \prod \Delta T$$

Here ΔP_s = spontaneous polarization

$\prod$ = Pyroelectric co-efficient

ΔT = change in temperature

That means spontaneous polarization depends upon temperature.An increase in temperature gives decrease in spontaneous polarisation. Polarisation suddenly falls to zero on heating above a particular temperature.

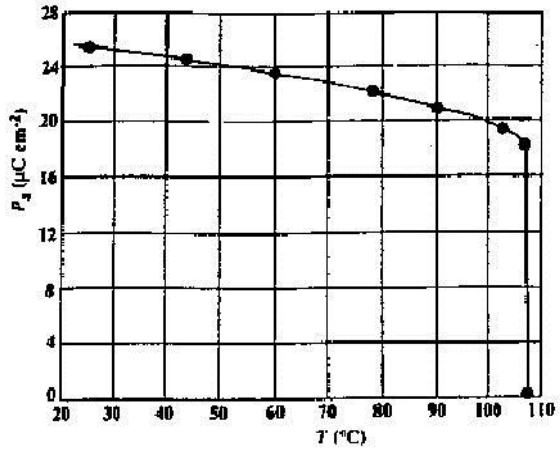

Fig. 1.2: The temperature dependence of spontaneous polarization Ps for $BaTiO_3$ ferroelectric crystal.

1.4 Pervoskite crystal structure:

Ferroelectric structure is of 4-types. i.e.

1. Pervoskite structure
2. Bismuth layer structure
3. Tungsten-Bronze structure
4. Pyrochlore structure

We generally use Pervoskite structure of material because it shows excellent dielectric property. The formula for pervoskite structure is ABO3. Where A is a mono- or divalent and B is a tetra- or pentavalent metal. In (Fig.1) the A atoms are in the corner of the cubic cell, B atoms are in the centre and the oxygen atoms are situated in the faces centres of the cubic cell and the lattice is centre of symmetry so here no ferroelectricity can be observed.

The ideal structure is cubic perovskite, where A and B cat ions are arranged on a simple cubic lattice and the O is the anion.

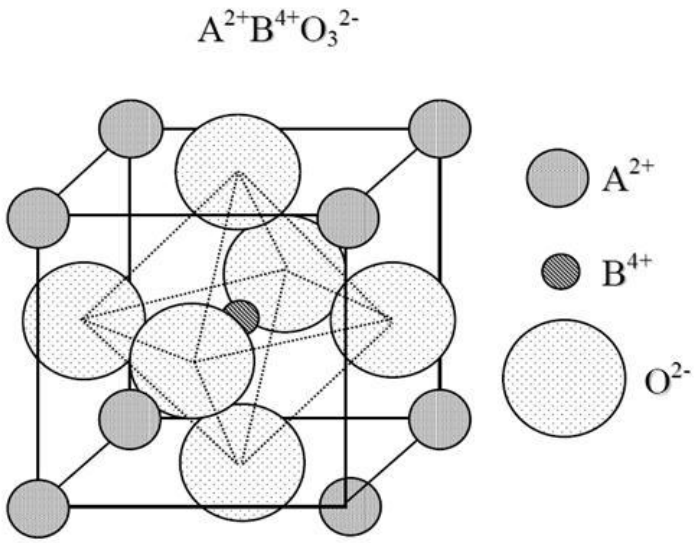

Figure 1.3 A cubic ABO3 perovskite-type unit cell.

1.5 Barium Titanate (BaTiO3**) :**

$BaTiO_3$-based solid solutions are environment-friendly dielectrics with similar performances as many Pb-based electro-ceramics. Recently, there has been continued growth of interest in

the use of $BaTiO_3$-based ceramics, because they are promising materials for tunable microwave device application such as electronically tunable mixers, delay lines, filters, capacitors, resonators and phase shifters. They possess the following properties which is required for device application

- High dielectric constant
- Large tunability;
- Low loss tangent
- And good thermal stability

Barium titanate (BT) is can be used in various forms, e.g. bulk, thin and thick films, powder, in a number of applications).it has a paraelectric cubic phase transition above its Curie point of about 130° C. Barium titanate is a ferroelectric ceramic material, with a photorefractive effect and piezoelectric properties. It has five phases as a solid, listing from high temperature to low temperature: hexagonal, cubic, tetragonal, orthorhombic, and rhombohedral crystal structure. All of the structures exhibit the ferroelectric effect except cubic.

1.6 Polymer composite

- Polymer composite is composites made from polymers or from polymers along with other kinds of materials.

- Polymer + Ceramic = polymer composite

Combination of both can overcome the drawbacks of each individual.

The composite materials are heterogeneous in nature. There has been a rapidly increasing search for the materials which can replace conventional material. Those ideal structural materials should have low densities, high tensile strength, and high stiffness. Polymer composite material is up to greater extend fulfilling the demand for such material. As the Fabrication of composite materials is nothing but the combination of two or more different materials having different properties to obtain the desirable material properties that often cannot be obtained in single-phase materials. Polymer has some merits and also some demerits. It has good mechanical property, easy to synthesis, low acoustic impedance, and high dielectric break down strength and the demerit is low dielectric constant. Like that ceramics have some merits and demerits. It has poor mechanical properties, high acoustic

impedance, and high dielectric constant and lower dielectric breakdown strength. When we add polymer with ceramic they we can overcome these problems. That means polymer composites have good mechanical properties, low acoustic impedance, intermediate dielectric constant and high breakdown strength. Polymer composites are in demand due to their potential application in batteries, electrochemical sensor, capacitor and transducer.

As we know in technical application the role of energy storage device have tremendous role like computers, communication devices, industrial controls, electric vehicles, space ships etc. Because of excellent mechanical, thermal stability and high ionic conductivity of polymer composite it is used for the said application.

CHAPTER -2

2.1 Motivation

Recent years have witnessed constant search for high permittivity materials that have wide range of technologically important applications such as microelectronic, embedded passive, and electrostrictive devices [1,2]. Majority of the electronic component in microelectronic circuits are passive and occupy more than 80% of the printed wired surface area. Integration of embedded passive components into printed circuit board offers a significant reduction in size, better electrical performance, reliability, lower cost and improved design options. Among embedded passive components, the embedded capacitor is particularly favorable because they are used in large number of various functions such as decoupling, bypassing, energy storage and filtering capacitors. One major challenge for implementing the embedded capacitor technology is the development of new dielectric material that possesses good dielectric and mechanical properties and process abilities.

2.2 Thesis objective:

The objective of my thesis is

- Preparation of Yttrium doped $BaZr_{0.1}Ti_{0.9}O_3$ (BZT) ceramic with general formula $Ba_{1-x}Y_{2x/3}Zr_{0.1}Ti_{0.}9O3$ (BYZT) by solid state method.
- Structural study of by XRD.
- Fabrication of polymer composite.
- Structural and Micro structural study of Polymer composite by XRD and SEM.
- Study of Electrical behavior of polymer composite by dielectric and impedance spectroscopy.

  Polyvinyl alcohol (PVA) used as polymer due to some excellent properties of polymers like it is a water soluble polymer, and it has excellent adhesive property. Also it has high tensile strength and flexibility.

CHAPTER-3

3. Experimental Techniques

Our aim is to prepare polymer ferroelectric composite. First ceramic powders are prepared and then by mixing these ceramics with polymer polymer composite are prepared. The general formula of the ceramic material is $Ba_{1-x}\ Y_{2x-3}\ Zr_{0.1}\ Ti_{0.9}\ O_3$ (BYZT). A site modified $Ba_{1-x}\ Y_{2x-3}\ Zr_{0.1}\ Ti_{0.9}\ O_3$ ceramics has synthesised with the dopant Yttrium (x=0, 0.01, 0.02, 0.03) by conventional solid state reaction method.

To understand the structural, electrical properties of a material used different characterization methods.

3.1 X-ray Diffraction Study:

As we know the physical properties of solid i.e. optical, electrical, magnetic, ferroelectric etc depends on atomic arrangements of materials so X-Ray Diffraction pattern (XRD) is a very important tool for material characterization. So for the determination of a structure of material and the fingerprint characterization of a material we are using XRD. When the highly energetic X-Ray beams strikes the atom of the crystal surface they scatter in different direction. In few directions these waves obey Bragg's condition.

$$\text{i.e } 2d \sin\theta = n\lambda$$

By XRD study we can know how the atoms are pack in the crystal, interatomic distance, angle, phase composition.

3.2 Scanning electron microscope:

SEM is used for the study of topographies, morphology and the composition of the material at high magnification. The principle of SEM is a highly energetic electron beam emitted from an electron gun fitted with a Tungsten filament cathode strikes the sample as a result the secondary electrons-Rays and back scattered electrons are ejected from the sample. These electrons convert into the signal and that displays on the screen. In SEM depth of field is so a large amount of the sample can be focus at one time. The image produce in SEM have very high resolution that means closely packed features can be examined at a high magnification.

3.3 Dielectric study:

To measure the capacitance, dissipation factor, and dielectric constant we need dielectric measurement. Dielectrics are such materials which are ideal insulators which would have no free electrons. A dielectric material has the interesting properties that of the ability of an electric field to polarize the material to create electric dipoles. The dielectric study is concerned with the storage and dissipation of electric and magnetic energy in material.

3.4 Impedance study:

The impedance $|Z|$ and the phase difference (θ) between the voltage and current are measured as a function of frequency for the given sample and the technique is called impedance spectroscopy. To study the electrical properties of the complex pervoskite material we generally use impedance spectroscopy. This involves very simple electrical measurements and the results we get can be correlated with the properties i.e. microstructure, defects, dielectric properties, chemical reaction etc .In this technique we can separate the grains and grain boundaries. Impedance plot takes place between the imaginary part of the impedance $Z''=|Z|cos\theta$ against the real part $Z'=|Z|sin\theta$ on a complex plane. The impedance can be expressed by the following relation $Z^* = Z' - jZ'' = R / 1+j\omega RC$

3.5 Preparation of ceramic powder:

For synthesis of $Ba_{1-x}\ Y_{2x-3}\ Zr_{0.1}\ Ti_{0.9}\ O_3$ (BYZT) the precursors are used Barium carbonate ($BaCO_3$), titanium oxide (TiO_2), Zirconium Oxide (ZrO_2) and Yttrium Oxide (Y_2O_3). All the precursors are having 99% purity. For the preparation of 20gms, the precursors are calculated in a stoichiometric ratio.

The precursors are mixed thoroughly in dry condition in an agate motor for 2hrs. For getting the homogeneous mixture used ball milling technique which is a grinding process. The process continued for 12 hrs in the liquid medium using isopropyl alcohol. Then the mixture is dried under IR lamp and again the powders were grinded in an agate motor for 15mins. The dried powders are kept in an alumina crucible for calcinations which is a process the material is heated to a temperature below its melting point to get the single phase and removal of volatile fraction. The calcination is carried out at 1350^0c for 4hrs and then cooled in the furnace. Again the calcined powders are grinded in an agate motor to get the fine powder and

those powders used phase formation study by XRD. Preparation of the ceramic is shown below in the flow chart.

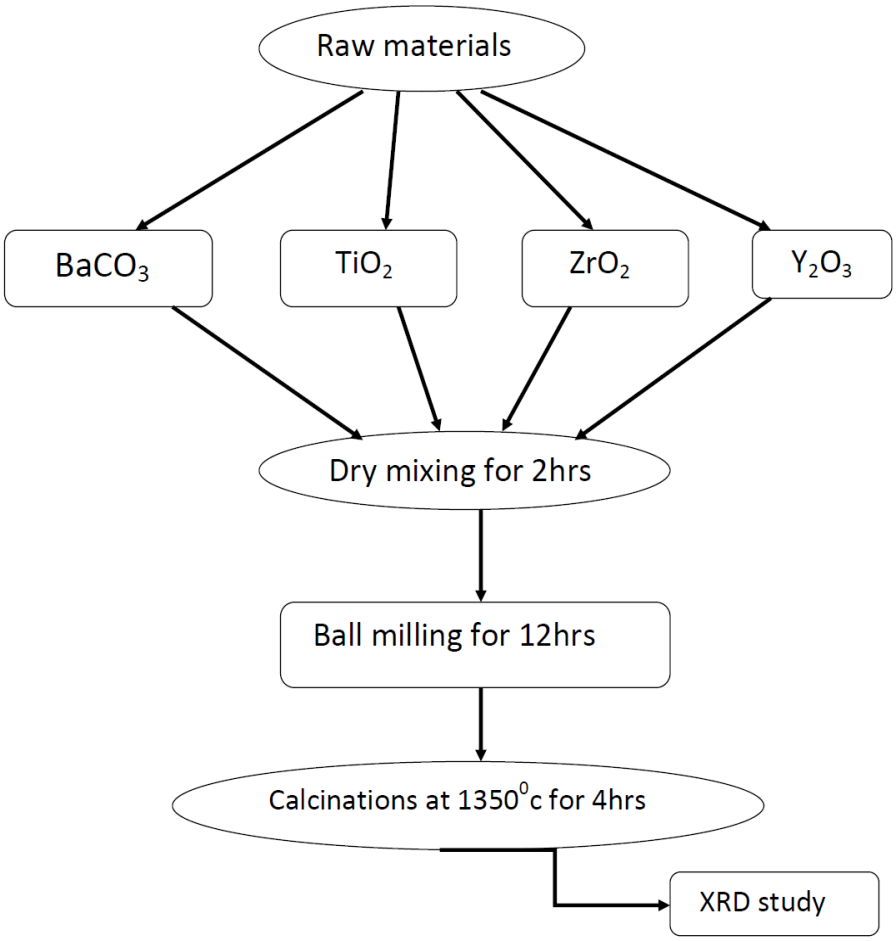

Fig. 3.1 Flow chart for the preparation of ceramics by solid-state route

3.6 Preparation of polymer composite:

To prepare the polymer ceramic composite, polyvinyl alcohol is used as polymer. The composition of polymer and ceramics were taken in the volume percentage ratio 100:0%, 75:25% and 50:50%.

For 100% composition

Polymer required = 1.28gm

Ceramic required = 0gm

For 75%+25% composition

Polymer required =0.96gm

Ceramic required = 1.505gm

For 50%+50% composition

Polymer required = 0.64gm

Ceramic required = 3.01gm

PVA dissolved in 20ml of distilled water in the hot condition. The solution is stirrered continuously at the temperature 80oC for 2hrs to get the gel condition. After the gel formation the ceramic mixed in volume percent ratio in the agate mortar under IR lamp for 15 mins. The mixed polymer and ceramic gel dried and become rubber like condition. Then that composition is dried in IR lamp and its subjected to hot press to make the thick film. The composite has hot pressed at 100oC for 2 mins using the pressure 5 tonns. Then to know the structural, micro structural, electrical behaviour of the composite the XRD, SEM and Dielectric and impedance studies has carried out.

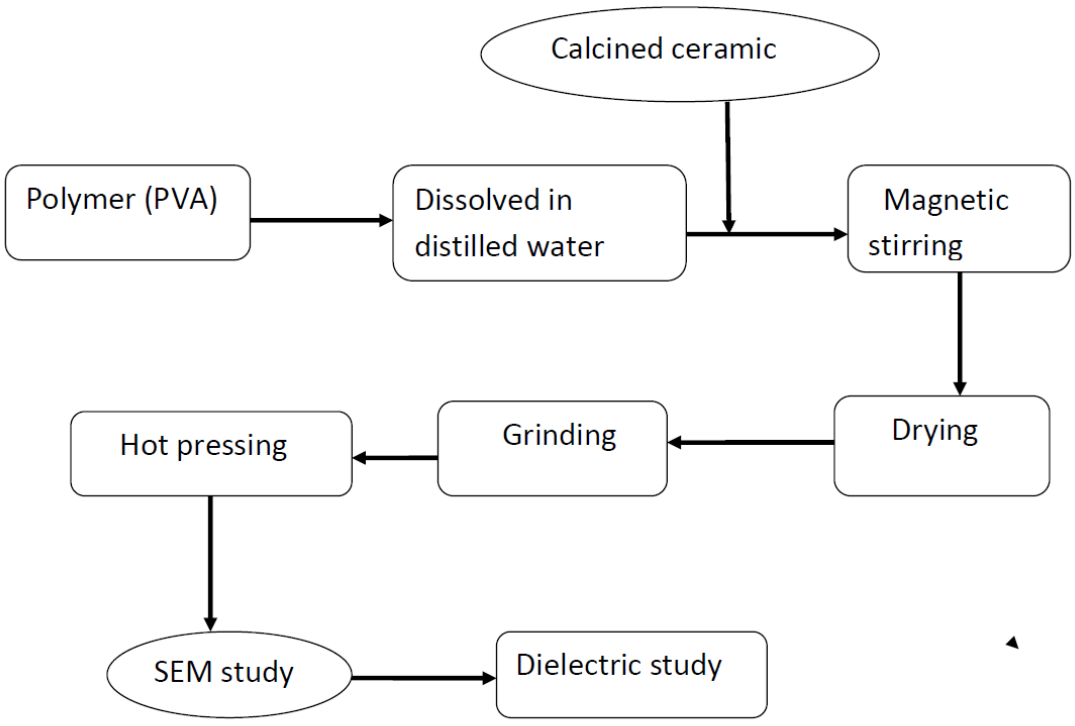

Fig 3.2: flow chart for the preparation of polymer composite

CHAPTER -4

4.1 INTRODUCTION ON BZT:

The lead-free ceramic oxides have been widely used due to their dielectric, ferroelectric, electromechanical and piezoelectric properties [3-8]. These materials do not present detrimental effects to human health and environment [9-11] besides the high thermal stability. Barium strontium titanate (Ba,Sr)TiO3 (BST) has been considered a promising material for the development of tunable microwave devices because it has strong electric field dependence of dielectric constant. But it has the drawback is dielectric loss at high frequencies [12-15]. The barium zirconate titanate Ba(ZrxTi1-x)O3 (BZT) has received more attention in the field of materials science by reason of its structural and physical properties exhibit a significant dependency with the titanium (Ti) and zirconium (Zr) contents into the matrix [16,17]. The dielectric properties as well as the phase transition from ferroelectric to relaxor focused with the perovskite structure [18-20]. In order to improve the electrical properties the BZT ceramics have been doped with different doping elements like lanthanides, semi-metal and alkaline-earth metals such as: niobium, boron, lithium, yttrium, copper, vanadium, manganese, tungsten, nickel, aluminium, lanthanum, bismuth and ytterbium. However, there are few studies reported in the literature on the optical properties of this compound. For example, Liu et al. [21] analyzed the infrared optical properties of BZT thin films prepared by the sol gel method, using only two Zr concentrations(x = 0.20 and 0.30) into the lattice. They observed that the refractive indexes (n) of these thin films are lower when compared with those of BaTiO3 single crystals in the wavelength range from 2500 to 12000 nm. In terms of photoluminescence (PL) measurements at room temperature, the BZT (thin films or powders) has shown typical blue and orange emissions. In general, phase the origin of the PL phenomenon has-been attributed to the degree of structural order disorder into the lattice, as a consequence of the symmetry break between the O-Zr-O and O-Ti-O bonds [22-25].Therefore, in this work, we report on the structure and optical properties of[Ba1-xY2x/3](Zr0.1Ti0.9)O3 powders synthesized with different yttrium (Y)concentrations(x=0.0.01,0.02and 0.03) by the solid state reaction method.

4.2 Result and discussion:

4.2.1 XRD of BYZT:

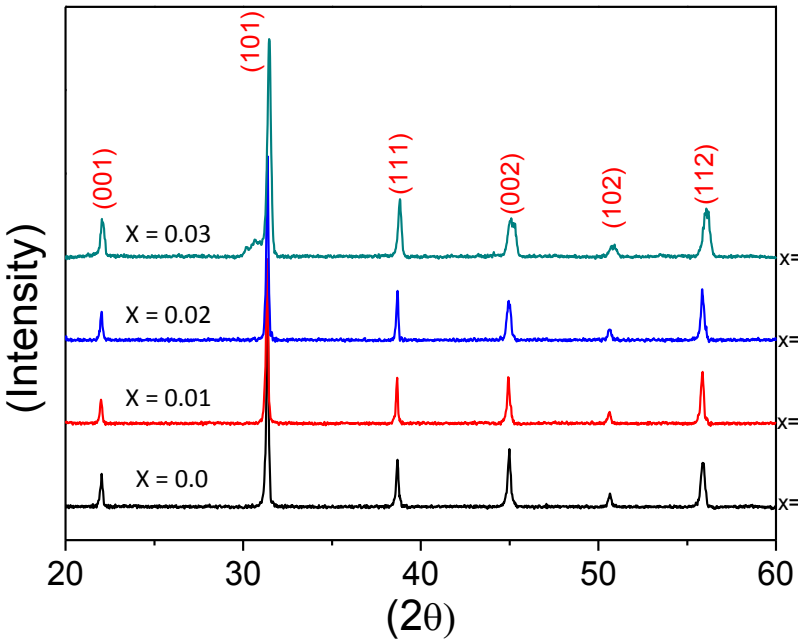

Fig 4.1 XRD pattern for BYZT ceramic

The above XRD patterns indicated that all powders are in a perovskite type cubic structure with space group Pm3m, in agreement with the respective Joint Committee on Powder Diffraction Standards (JCPDS) card No. 36-0019. Diffraction peaks related to the Y2O3 (secondary phase) were not detected in the composition upto x = 0.02, suggesting that the Y atoms were incorporated into the [Ba1-xY2x/3] (Zr0.1Ti0.9) O3 structure. But in the x = 0.03 composition shows the some impurities (secondary phase) in the XRD pattern. The substitution of Y in Ba sites leads to the distortions into the BZT structure because of the different atomic radii. The literature reports that the ionic radius of Ba2+ ions is approximately 0.161 nm, while those of Y3+ are 0.086 nm. Based on these hypotheses, we suppose that the substitution of Ba sites commonly occupied by Y atoms causes an electronic compensation through the formation of barium vacancies (VBa^{x}, VBa' or VBa"). In this case, it is very probable that the Y atoms are coordinated to six oxygen (O) atoms (distorted [YO6] clusters), while the Ba atoms are bonded to twelve oxygen atoms ([BaO12] clusters). Hence, the substitution processes of [BaO12] by distorted [YO6] clusters

CHAPTER-5

5.1 Polymer composite:

Electronic systems in general consist of both the active and passive components. The technologies concerning the development of the passive components such as resistors, inductors, and capacitors are steadily growing in the electronic industries. Among these passive components, the capacitor is the one which attracts special attention due to its variety of functions that include decoupling, by-passing, filtering and timing capacitors. In recent years much work has been done on polymer–ceramic composites. Owing to the continuous development towards the miniaturization of electronics, high dielectric constant polymer–ceramic composites have become promising materials for embedded capacitor applications. Ferroelectric ceramics possessing very high dielectric constants are brittle and suffer from poor mechanical strength.

On the other hand, polymers having low dielectric constants are flexible, easy to process and possess high dielectric strength. New composites associated with high dielectric constant, and high dielectric breakdown strength to achieve high volume efficiency and energy storage density for applications of capacitors and electric energy storage devices could be fabricated by combining the merits of polymers and ceramics.

Polyvinyl alcohol (PVA) is a good insulating material with low conductivity and hence is of importance to microelectronic industry. It electrical conductivity depends on the thermally generated carriers and also on the addition of suitable dopants [26,27]. Although charge transport in polymers is a problem with great technological implication, the current understanding of the elemental processes involved is still unsatisfactory [28]. In the present work an attempt has been made to study the electrical transport properties of pure PVA films and doped films of PVA with carbon black using aluminium and gold as ohmic and blocking electrodes respectively.

Polymer–ceramic composites combine superior properties of both polymer and ceramics which results in far better performance than those of the constituent materials. Polymers are flexible, easy to fabricate and superior in dielectric break down strength. On the other hand, ferroelectric ceramics possess high dielectric permittivity but with poor mechanical properties and lower dielectric breakdown strength [29]. By integrating high dielectric permittivity ceramic powder with superior dielectric strength of the polymer, one can develop a composite

with high dielectric permittivity and high breakdown strength. This type of composites has high capability of energy storage and can be used in capacitors and energy storage devices. The easiness of composite fabrication allows producing thin film capacitors which is difficult to achieve in ceramics due to complicated fabrication routes.

5.2 Result and Discussion

5.2.1 XRD of polymer composite

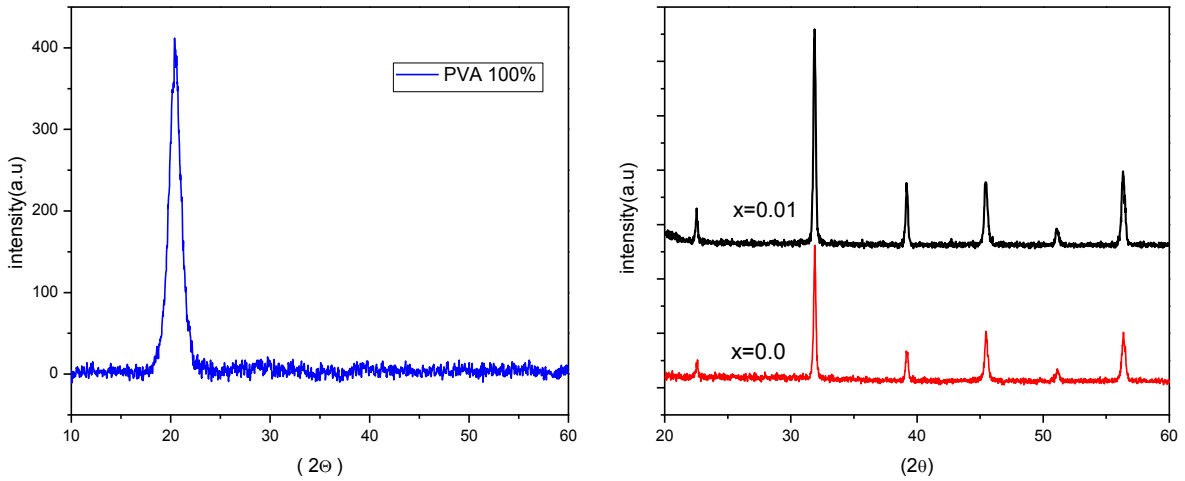

Fig 5.1: XRD of polymer composite (a) PVA-BYZT100:0% and (b) PVA-BYZT75:25%

To investigate the influence of ferroelectric on polymer structure, X-ray diffraction studies were performed for pure PVA and BZT based ferroelectric ceramic (Fig. 5.1). A broad peak at 21° was observed in pure PVA films, and this can be attributed to the semi crystalline behaviour of the polymer corresponding to the orthorhombic lattice structure. It is evident from the figure that there is a relative decrease in the intensity of this peak with the increase of dopant concentration. This may be due to the increase of amorphous nature of PVA with the addition of ferroelectric ceramic.

5.2.2 SEM of Polymer Composite:

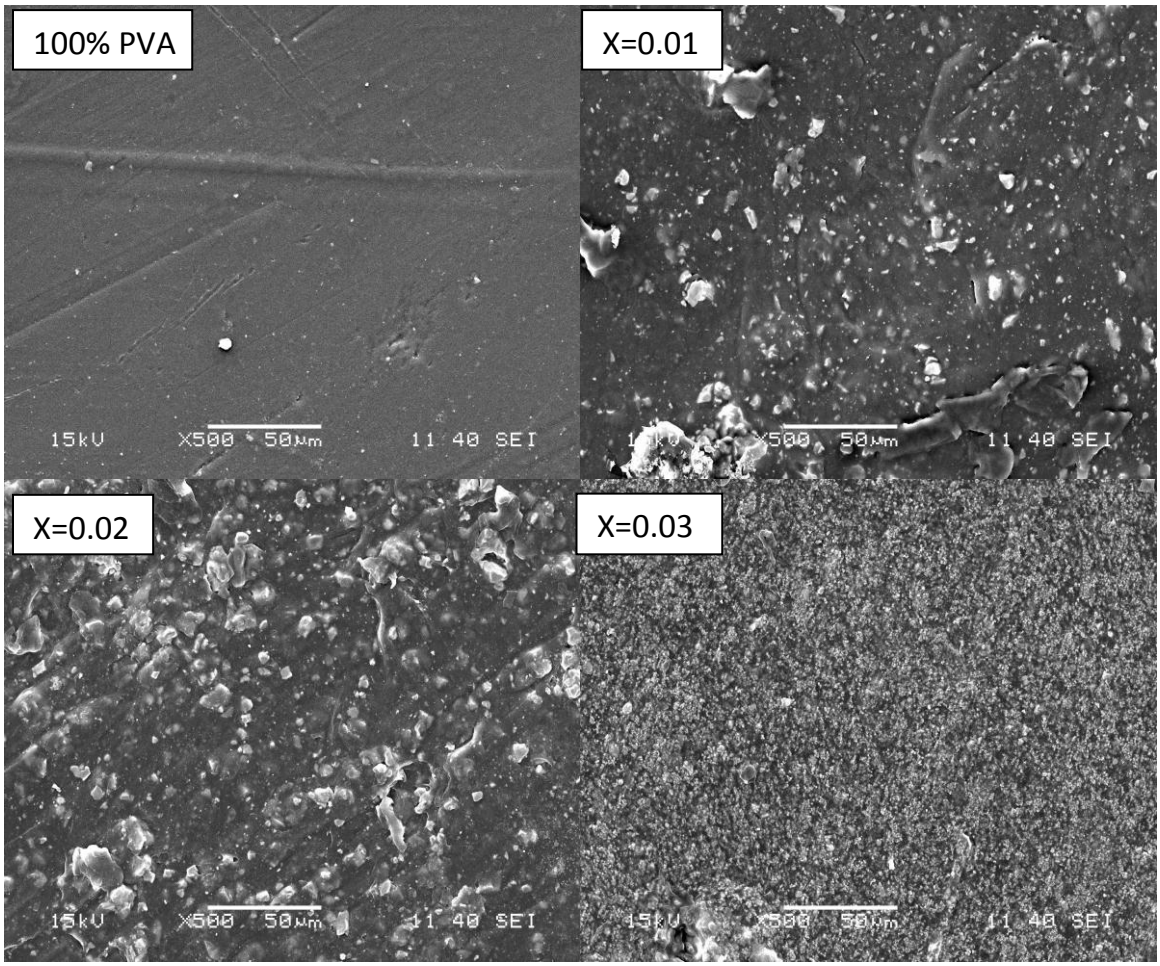

Fig 5.2 SEM images of the polymer composite thick films

Scanning electron microscopy (SEM) is often used to study the compatibility between various components of the polymer electrolytes through the detection of phase separations and interfaces. The compatibility between the polymer matrix and the inorganic dopants has great influence on the properties (mechanical, thermal, ionic conductivity) of the polymer electrolytes. The morphology of the pure PVA and PVA/BSZT 100:0% and 75:25% polymer electrolytes, studied by SEM technique, is a uniform type but with different degrees of roughness (Fig. 5.2). However in case of the composite the ferroelectric ceramic oxides are distributed homogenously on the polymer matrix. In SEM micrographs of the composites, the bright area corresponds to the ferroelectric ceramics and the dark region corresponds to the polymer matrix.

5.2.3 Dielectric study

5.2.3.1 Temperature dependence of dielectric constant

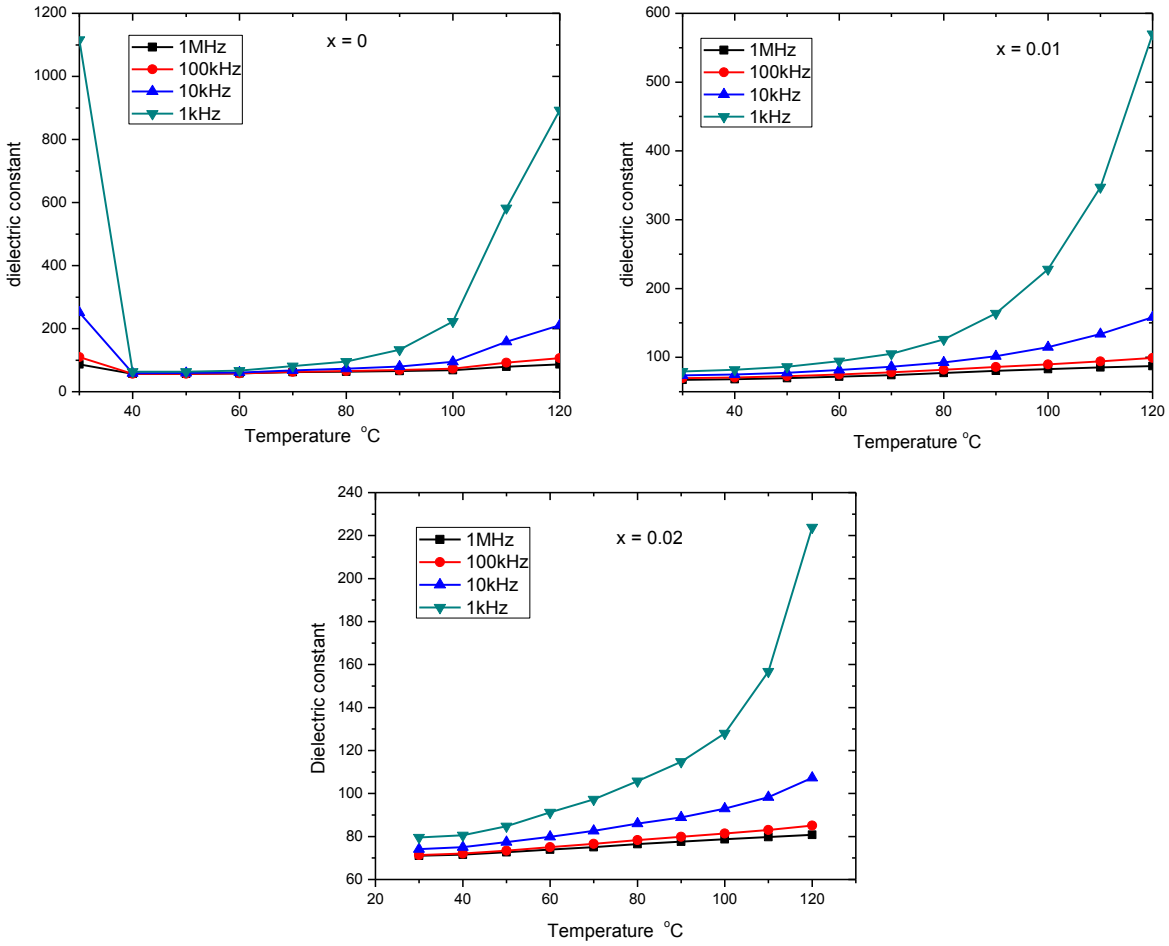

Fig 5.3. Temperature dependence of Dielectric constant of the polymer composite for different frequencies

The temperature dependences of the dielectric properties of PVA-BYZT (75:25%) at different frequency fields are illustrated in Fig. 6. As shown in Fig. 6, the dielectric constant gradually increased with increasing temperature. This observation is in other polymer/BaTiO3 composites, where the ε' increased with temperature [29,30]. Generally, the change of dielectric property in the composites includes three competitive mechanisms: (a) the segmental mobility of polymer would improve with increasing temperature, which should facilitate the polarization of polar components and increase the dielectric constant consequently, (b) the thermal expansion of polymer could disrupt the chains of contact BaTiO3 particles, which should reduce the dielectric constant and (c) the structure of BaTiO3 particles could be changed with an increase in temperature (before Curie temperature), which

could generate a modification on the dielectric response of the ceramic [31]. According to the above literature, the dielectric constant is increased in the polymer composite of PVA-BYZT. Due to the dopant increment, the frequency dispersion is observed more compared to the undoped BZT sample. And also, as the earlier report [32], dielectric constant is decreased with increasing Y concentration. This is may be the effect of oxygen vacancies as explained in the XRD report.

5.2.3.2 Frequency dependence of dielectric constant

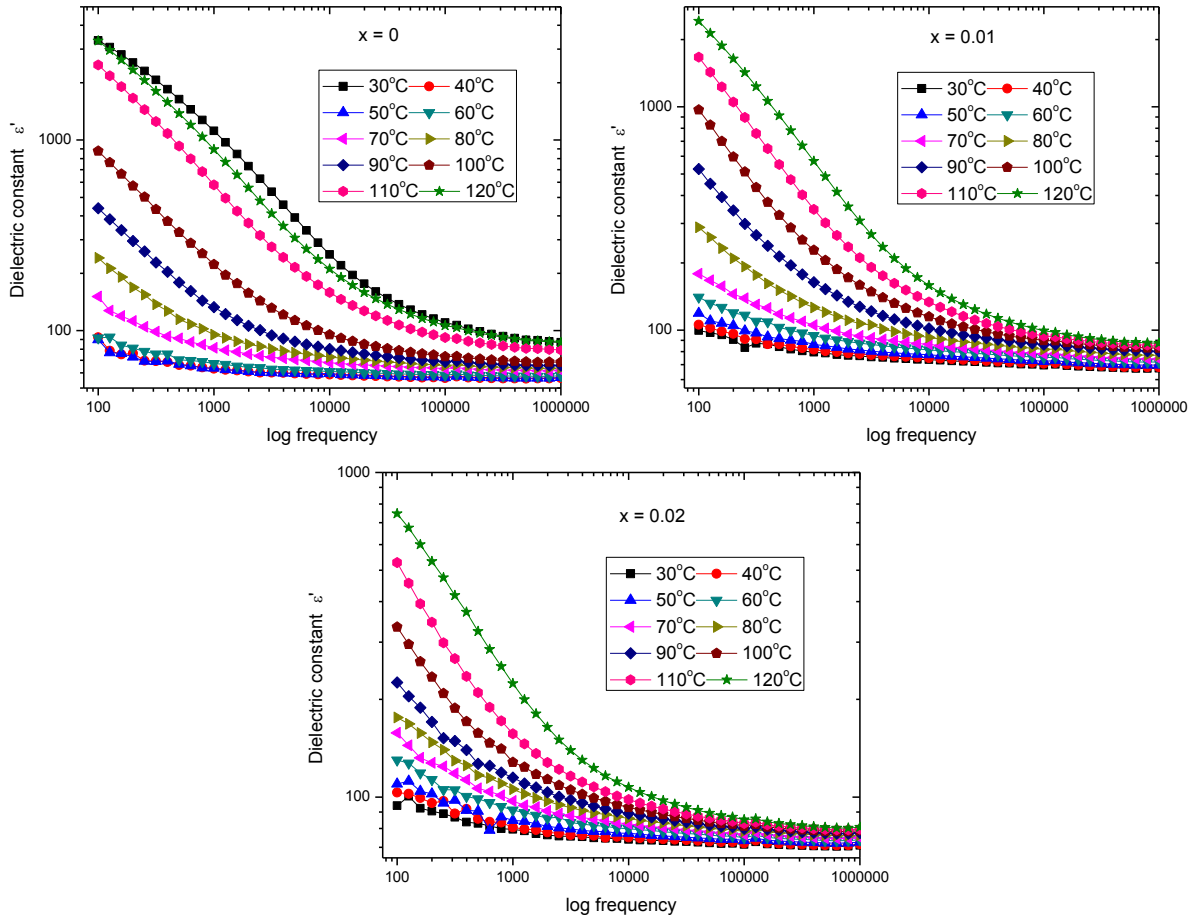

Fig 5.4 Frequency dependence of Dielectric constant of the polymer composite for various temperatures

Figure 5.4 shows the variation of the dielectric permittivity with frequency for the PVA:BYZT (75:25%) polymer electrolyte at different temperatures. From the plots, it is clear that the permittivity decreases monotonically with increasing frequency and attains a constant value at higher frequencies. Similar behavior has also been observed in other materials. This

is because, for polar materials, the initial value of the dielectric permittivity is high, but as the frequency of the field is raised the value begins to drop, which could be because the dipoles are not able to follow the field variation at higher frequencies, as well as polarization effects. The low-frequency dispersion region is attributed to charge accumulation at the electrode–electrolyte interface. At higher frequencies, the periodic reversal of the electric field occurs so fast that there is no excess ion diffusion in the direction of the field. Hence, the dielectric permittivity (ε′) decreases with increasing frequency in all of the samples. the measured series capacitance, Cs is given by

$$C_S = C' + \frac{1}{\omega^2 R^2 C'}$$

where C′ is the frequency-independent capacitance, R is the temperature-dependent resistance, and ω is 2πf. The above equation predicts that Cs should be decrease with increasing frequency f, eventually tending to a constant value C′ for all temperatures and any given frequency. Since the permittivity is directly proportional to C_s,

$$C_s = \varepsilon A/d$$

where d is the thickness of the film and A is the effective area (contact area of the electrode during the experiment), the permittivity should decrease with increasing frequency

5.2.3.3 Frequency dependence of dielectric loss

In all the compositions, the loss peaks shows high values in low and high frequencies and the small down curve in the middle of the frequencies. The down curve is shifted to higher frequencies with increasing temperature and it disappears in high temperature for x=0 composition. For doped compositions, the down curves are in the experimental frequency range. This curve like structure may give two relaxation process in low frequency side and high frequency side beyond the experimental limit as reported earlier sengwa and choudhary [33].

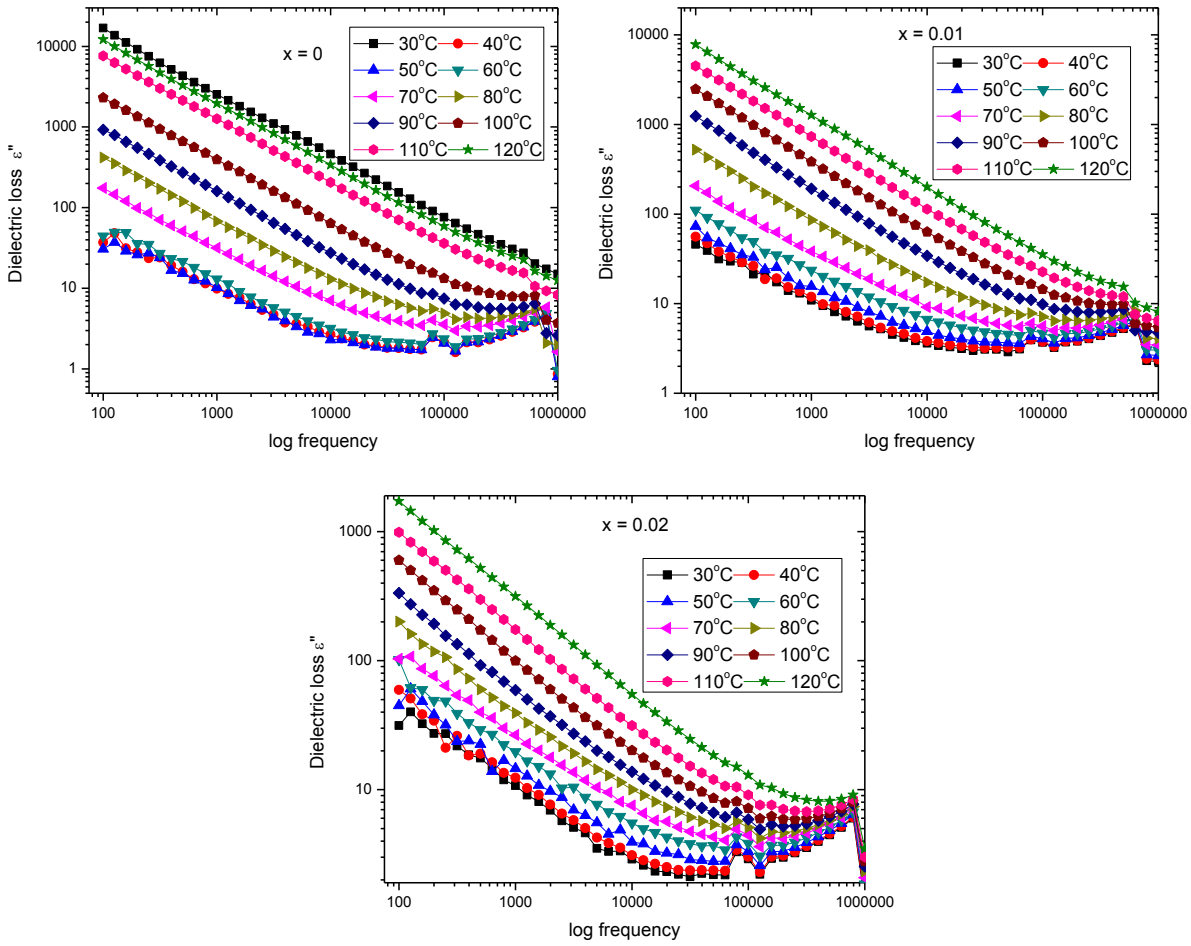

Fig 5.5 Frequency dependence of Dielectric loss of the polymer composite for various temperatures

5.2.3.4 Complex Impedance spectroscopy

In order to carry out a more detailed analysis of dielectric properties the temperature dependence impedance spectroscopy is used. It is necessary to understand the contribution of grain, grain boundary and sample interface effects, which greatly influence the properties. Conventionally, the bulk and grain boundary contributions to the overall impedance can be resolved by exploiting differences in their responses to an alternating applied field. Normally ceramic samples will show a Poly-dispersive non-Debye type relaxation, due to which the complete semicircle of the complex impedance data will show in a depressed manner (i.e., centre of the semicircle lie below the real axis).

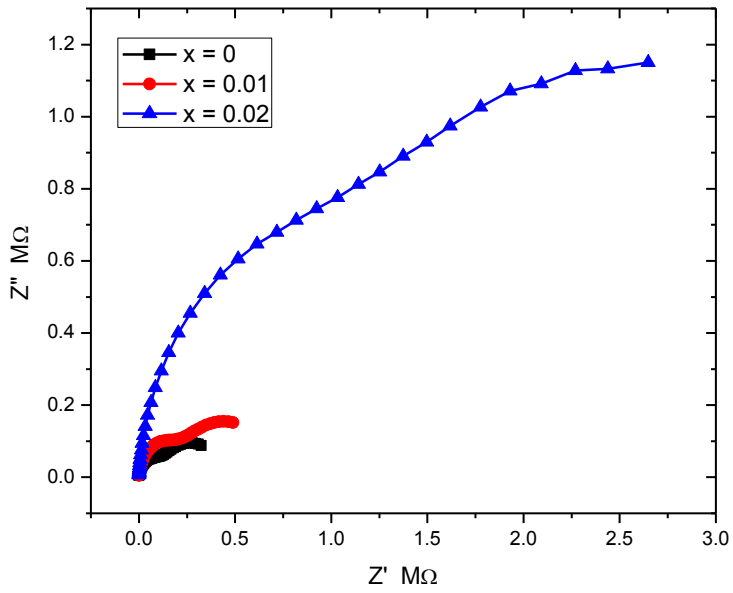

Fig.5.6 Complex impedance plot of polymer composites at 102^{o}C

Fig. 5.6 shows the Nyquist plots (complex impedance spectrum) of polymer composite at different temperatures. This plot shows the transport response function. Characteristically, one semicircular arcs have been observed at low temperatures and second circles slowly formed for high temperatures. At 120^{o}C, complete two semicircles are formed and the low frequency semicircle is considered due to the grain boundary (blocking core) whereas the higher frequency semicircle depicts the bulk effect. This bulk effect arises due to the parallel combination of bulk resistance *(R_b)* and bulk capacitance *(C_b)* of polymer composite. This plot indicates the changes in grain boundary resistance at elevated temperatures representing the role of grain boundaries in electrical conduction process of the material. Doped samples shows the high values of grain and grain boundary resistance compared to the undoped samples at particular temperature 120^{o}C. In the overall temperature range (fig not shown) grain boundary resistance decreases with rise in temperature may be due to the lowering of barrier favoring the increase of mobility of charge carriers that adds to the conduction process.

CHAPTER -6

Conclusion

In this work, we have prepared and studied the perovskite ceramics having the general chemical formula$Ba_{1-x}Y_{2x/3}Zr_{0.1}Ti_{0.9}O_3$, and the composite of PVA and BZT. The structural (XRD), micro structural/morphological and electrical properties of the proposed compounds have been extensively studied.

Based on our results following conclusions have been drawn.

- The polymer composite ferroelectric material is prepared by conventional solid state reaction method taking PVA as a polymer matrix.
- The X-ray diffraction patterns of the Y^{2+} substituted BZT powders and polymer composite, it can be clearly seen that for all Y contents single phase BZT compound has been observed without the presence of any impurity peaks.
- SEM micrographs shows that the BYZT particle distribution is homogenous with no porous in the PVA matrix.
- The dielectric study shows that the prepared polymer composite materials have high dielectric constant value showing ferroelectric behavior.

References

[1] Chen F, Chu C, He J, Yang Y, Lin J. Organic thin-film transistors with nanocomposite dielectric gate insulator. Appl Phys Lett 2004;85(15):3295–7.

[2] Rao Y, Ogitani S, Kohl P, Wong CP. Novel polymer–ceramic nanocomposite based on high dielectric constant epoxy formula for embedded capacitor application. J Appl Polym Sci 2002;83(5):1084–90

[3] P. Kantha, K. Pengpat, P. Jarupoom, U. Intatha, G. Rujijanagul, T. Tunkasiri, Curr. Appl. Phys. 9 (2009) 460.

[4] C. Peng, J.F. Li, W. Gong, Mater. Lett. 59 (2005) 1576.

[5] D. Lin, K.W. Kwok, H.L.W. Chan, Mater. Chem. Phys. 109 (2008) 455.

[6] H. Maiwa, Jpn. J. Appl. Phys. 46 (2007) 7013.

[7] Z. Zhang, J. Jia, H. Yang, C. Chen, H. Sun, X. Hu, D. Yang, J. Mater. Sci. 43 (2008) 1501.

[8] Z. Chen, J. Hu, Ceram. Inter. 35 (2009) 111.

[9] M.Z.C. Hu, V. Kurian, E.A. Payzant, C.J. Rawn, R.D. Hunt, Powder Technol. 110 (2000) 2.

[10] Z. Chen, A. Shui, Z. Lu, P. Liu, J. Ceram. Soc. Japan 114 (2006) 857.

[11] T. Maiti, R. Guo, A.S. Bhalla, J. Am. Ceram. Soc. 91 (2008) 1769.

[12] J. Cui, G. Dong, Y. Wang, J. Du, J. Mater. Sci: Mater. Electron 20 (2009) 473.

[13] J. Zhang, J. Zhai, X. Chou, J. Shao, X. Lu, X. Yao, Act. Mater. 57 (2009) 4491.

[14] M. Makimoto, S. Yamashita, Microwave Resonators and Filters for Wireless. Springer, 2001, (Chapter 1), pp. 5.

[15] M.T. Sebastian, Dielectric Materials for Wireless Communication. Elsevier, 2008, (Chapter 3), pp. 58.

[16] H. Khemakhem, A. Simon, R. von der Mhll, J. Ravez, J. Phys.: Condens. Matter 12 (2000) 5951.

[17] A. Simon, J. Ravez, Solid State Sci. 5 (2004) 1459.

[18] T. Tsurumi, Y. Yamamoto, H. Kakemoto, S. Wada, H. Chazono, H. Kishi, J. Mater.Res. 17 (2002) 755.

[19] X. Chou, J. Zhai, J. Sun, X. Yao, Ceram. Intern. 34 (2008) 911.

[20] C. Fu, F. Pan, W. Cai, X. Deng, X. Liu, Mater. Scie. Poland 27 (2009) 891.

[21] A. Liu, J. Xue, X. Meng, J. Sun, Z. Huang, J. Chu, Appl. Surf. Sci. 254 (2008) 5660.

[22] L.S. Cavalcante, M. Anicete-Santos, J.C. Sczancoski, L.G.P. Simões, M.R.M.

C. Santos, J.A. Varela, P.S. Pizani, E. Longo, J. Phys. Chem. Solids 69 (2008) 1782.

[23] L.S. Cavalcante, M.F.C. Gurgel, A.Z. Simões, E. Longo, J.A. Varela, M.R. Joya, P.S. Pizani, Appl. Phys. Lett. 90 (2007) 011901.

[24] S.K. Rout, L.S. Cavalcante, J.C. Sczancoski, T. Badapanda, S. Panigrahi, M. Siu Li, E. Longo, Physica B 404 (2009) 3341.

[25] L.S. Cavalcante, J.C. Sczancoski, F.S. De Vicente, M.T. Frabbro, M. Siu Li, J.A. Varela, E. Longo, J. SoleGel Sci. Technol. 49 (2009) 35.

[26] Mehendru, P.C., K. Pathak, K. Jain, P. Mehendru,Phys. 1997. Stat. Sol. 1(42): 403.

[27] Shinka, H.C., I.M. Talwar and A.P. Srivastava, 1989. Thin Solid Films, 82: 229.

[28] Bassler, H., 1984. Phil. Mag. B., 50: 347.

[29] Das-Gupta DK, Zhang S. Non polar polymer/ferro and antiferroelectric ceramic composite films for high energy storageapplications. Ferroelectrics 1992;134:71–7.

[30] Y. Rao, J. Yue, C.P. Wong, Proc. 51st IEEE Conf. Electronic Component Technology, 5th May–6th June, 2001, p. 1408.

[31] C.K. Chiang, R. Popielarz, Ferroelectrics 275 (2002) 1.

[32] L. Ramajo, M. Reboredo, M. Castro, Composites Part A 36 (2005) 1267.

[33] Badapanda et al., Materials Chemistry and Physics 121 (2010) 147–153

[34] Sengwa and Choudhary, eXPRESS Polymer Letters. 4 (2009) 559.